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Ortho and Paratritium*
by

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ABSTRACT

The conversion of ortho-paratritium in the homogeneous gas and solid phases are reported. The extent of conversion was measured by a heat conductivity cell cooled with liquid neon. The gas phase conversion was observed at the temperature of liquid neon where the equilibrium concentration is one part ortho to one part paratritium. The role of an ion mechanism in this conversion is discussed. For the solid phase conversion the rate is two orders of magnitude faster than the rate for hydrogen. Consideration of the kinetic data for hydrogen, deuterium and tritium in the solid phase and adsorbed phase indicates that a more favorable energy transfer process may be operative for tritium and deuterium.

Introduction

In normal hydrogen, due to the existence of the ortho and para modifications, in addition to the different physical properties, some basic reactions could be investigated; $H + H_2(\text{para}) \rightarrow H + H_2(\text{ortho})$

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(1,2,3) or parahydrogen forming normal hydrogen induced by ionizing

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- (1) K. F. Bonhoeffer and P. Harteck, Z. f. physikal. Chemie, B, 4, 113 (1929).
 - (2) A. Farkas, Z. f. Elektrochemie, 36, 782 (1930); Z. f. physikal. Chemie, B, 10, 419 (1930)
 - (3) K. H. Geib and P. Harteck, *ibid.*, Bodensteinband, 849 (1931).
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radiation.^(4,5) After the discovery of deuterium⁽⁶⁾, in addition to the

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- (4) P. C. Capron, Ann. soc. sci. Bruxelles, 55, 222 (1935).
 - (5) H. Eyring, J. O. Hirschfelder and H. S. Taylor, J. Chem. Phys., 4, 479, 570 (1936).
 - (6) H. C. Urey, F. G. Brickwedde and G. M. Murphy, Phys. Rev., 39, 164, 864 (1932).
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ortho-paradeuterium system, the chemical exchange between hydrogen and deuterium could be studied. At first glance one might be therefore lead to believe that very little new or basic knowledge could be acquired by investigating the ortho-paratritium system. But on the contrary more refined kinetic understanding may be achieved by the investigation of the ortho-paratritium system and mixtures of tritium with hydrogen and deuterium than could be achieved with hydrogen and deuterium alone.

In an earlier paper⁽⁷⁾ the conversion of normal tritium into

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- (7) E. W. Albers, P. Harteck, and R.R. Reeves, Zeitschrift Fur Naturforschung, 18a, 197 (1963).
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paratritium was reported using a coconut charcoal as a catalyst. The conversion of the normal tritium (three parts ortho and one part paratritium) was made at liquid neon temperature (27.2°K), obtaining the equilibrium concentration of 50% paratritium. By cooling the charcoal

with liquid helium practically 100% paratritium could be obtained. The concentration of paratritium was measured by the heat conductivity method of Bonhoeffer and Harteck^(1,8). The measured forward and reverse

(8) K. Bonhoeffer and P. Harteck, Sitzber. Preuss. Akad. Wiss. 103, (1929); Naturwiss. 17, 182. (1929)

processes at the boiling point of liquid neon and the boiling point of liquid nitrogen gave half lifetimes on coconut charcoal of 0.92 and 1.0 minutes respectively. This was an order of magnitude faster than expected when compared with the rate of conversion of normal hydrogen on the same charcoal under identical conditions as will be discussed later.

Conversion was also obtained without a catalyst by freezing the tritium with liquid helium. This solid phase conversion occurred with a seventeen minute half lifetime which was two orders of magnitude faster than expected.

Since tritium is radioactive, emitting beta particles with a half life of 12.5 years⁽⁹⁾ and an average energy of 5.69 kev. the

(9) L. Alvarez and R. Cornog, Phys. Rev., 56, 613 (1939); 58, 197 (1940).

possibility of ion reactions must be considered for the transformation of ortho and paratritium. It appears as will be discussed later, that the ions do not play an important part in the ortho-para conversion on charcoal, but causes conversion in the gas phase. The effect of the ions on the solid conversion needs to be investigated further.

Experimental

In the conversion experiments of normal hydrogen to para-hydrogen, measurements could be made each time with a fresh charge of

hydrogen which was then discarded. Because of the radioactive nature of tritium, however, it was not possible to follow exactly this same technique. Instead a sealed Pyrex apparatus was fabricated as a single unit within which one could convert the tritium to paratritium and back again to normal tritium, measuring the degree of conversion by the heat conductivity method in the closed system as used by Bonhoeffer and Harteck⁽⁸⁾. Prior to filling the apparatus with tritium, it was baked out at 170°C under vacuum for sixteen hours. Tritium was then admitted until the final pressure reached 1 mm, which corresponded to 300 millicuries. A schematic drawing is shown in Figure 1. The small bulbs D and J contained the catalyst (about one-tenth gram) for the conversion experiments. Bulb D contained a coconut charcoal, and bulb J a charcoal with a coating of gadolinium chloride to increase the number of paramagnetic centers substantially over that of ordinary charcoal. These tiny bulbs were connected with the apparatus by one millimeter capillary tubing (C) to minimize back diffusion. Unhindered back diffusion of tritium to the catalyst in the bulbs D and J at room temperature might result in reconversion of paratritium to normal tritium interfering with concentration measurements.

The overall size of the apparatus was approximately 280 mm x 250 mm x 20 mm. The ortho-paratritium concentration was measured by the heat conductivity cell, G, which was cooled with liquid neon, F, and jacketed with liquid nitrogen, E. The cell was made of 19 mm O.D. medium-wall Pyrex. The lead-in wires, H, were 22 gauge tungsten. A platinum filament approximately 100 mm in length and 10 microns in diameter, was soldered to the tungsten. This proved to be a suitable arrangement for studying the kinetics for the conversion on charcoal.

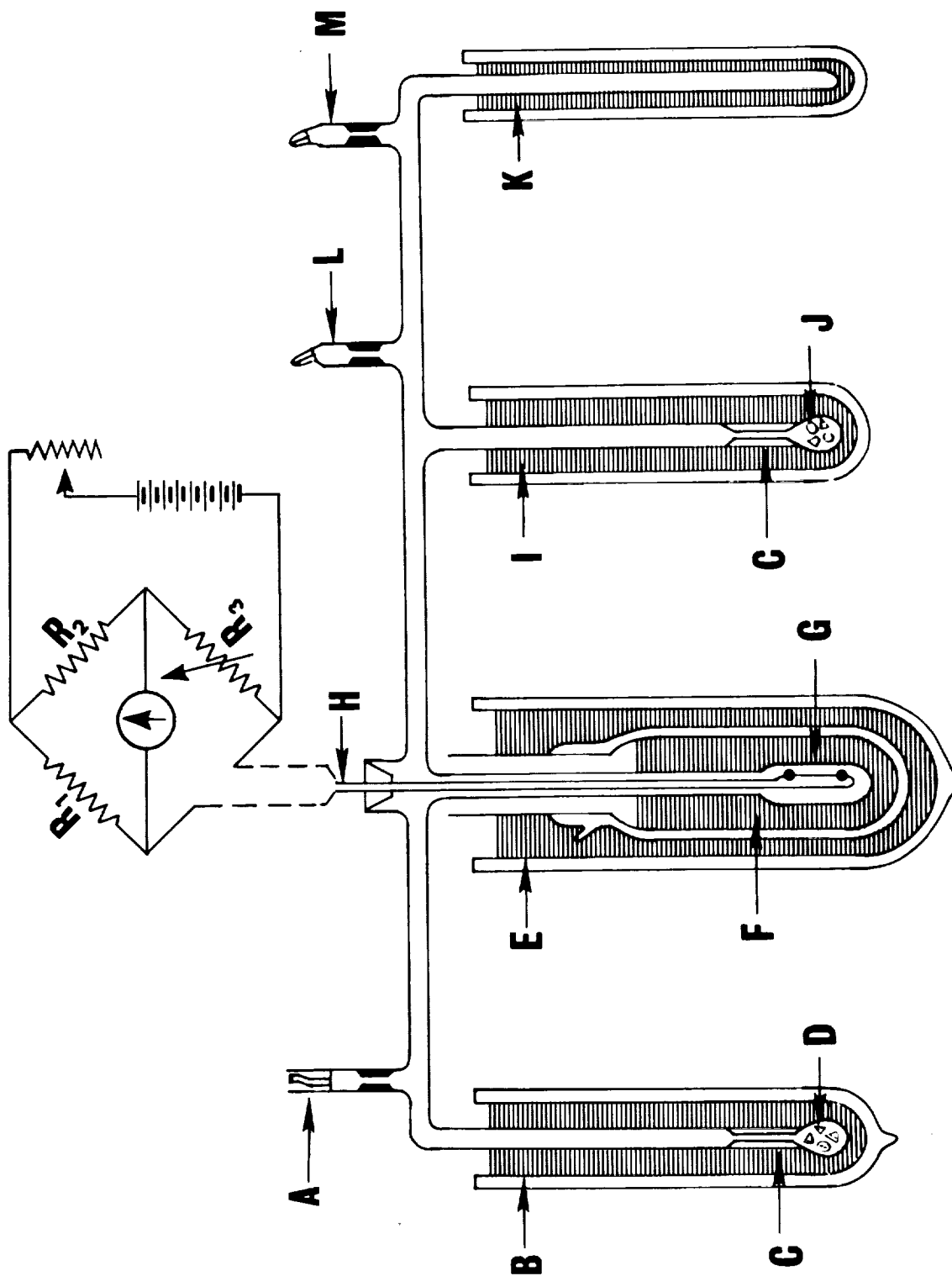


Figure 1

At the low pressures used the heat conductivity cell operated also to a certain extent as a Pirani gauge, which means that it will be sensitive to pressure changes as will occur when the level of the liquid neon decreases or if the room temperature changes. This becomes important if transformation phenomena are investigated which occur over a longer period of time since slight changes of the liquid neon level or changes in room temperature will correspondingly vary the pressure, effecting the reading of the gauge and therefore care must be taken to avoid undue errors.

At the start of a given series of measurements, the tritium was always first equilibrated to the normal tritium of 3 parts ortho-tritium to one paratritium by adsorbing it on the coconut charcoal at liquid nitrogen temperature.* After a few preliminary measurements it was apparent that ten minutes on charcoal was sufficient for equilibration. The tritium was then desorbed from the charcoal by heating the sample with boiling water. This procedure was followed by measurement of the resistance with the Wheatstone bridge to obtain the reference point of normal tritium on the thermal conductivity cell. For the determination of the conversion rate into paratritium the charcoal was first precooled with liquid nitrogen for two minutes. The nitrogen was then quickly replaced with liquid neon. It was anticipated that the neon temperature was reached in a few seconds and therefore at this point the conversion started. At the end of the predetermined time, the neon was removed and the tritium rapidly desorbed from the charcoal bulb with boiling water. The thermal conductivity of the tritium was then measured to determine the extent of conversion. The tritium was

*Theoretically 2.95 to 1 at 77.4°K

then re-equilibrated to normal tritium by adsorption for 10 minutes on charcoal at the temperature of liquid nitrogen as described before and the process repeated for different times to obtain the results in Figure 2. Equilibrium conversion at neon temperature was assumed to correspond to the resistance change observed for long cooling times (ten times or more adsorption time). It should be noted that tritium is almost at the normal equilibrium of 75% ortho to 25% para at liquid nitrogen temperature (77.4°K) and 52.5% ortho to 47.5% para at equilibrium for neon temperatures (27.16°K). See Table I.

In order to study the effect of ions in the gas phase a modified apparatus was constructed where an electric field could be applied within the cell. In Figure 3 a schematic drawing is shown for this arrangement. Bulb (A) contains approximately 0.5 grams of coconut charcoal. As before a one-millimeter capillary section (B) was incorporated to minimize back diffusion. The septums (C), (D), (E) were used for baking out, filling, and final disposal. Septum (G) shown in the sealed condition was used for evacuating the space containing the 38 gauge copper lead wires. The region noted by (F) simply indicates the physical arrangement which proved to be practical for the five 22 gauge nickel leads. Number 38 gauge copper leads were then soft soldered to their respective nickel leads at the top and bottom of this section. The filaments labelled (K) were two-micron diameter platinum Wollaston wires. Only one wire was used during measurements; the second was a spare since we were working with a sealed system.

In order to produce an electric field within the heat conductivity cell it was plated with two electrodes by depositing platinum metal on the inside wall in two strips 12.5 cm x 7 mm.

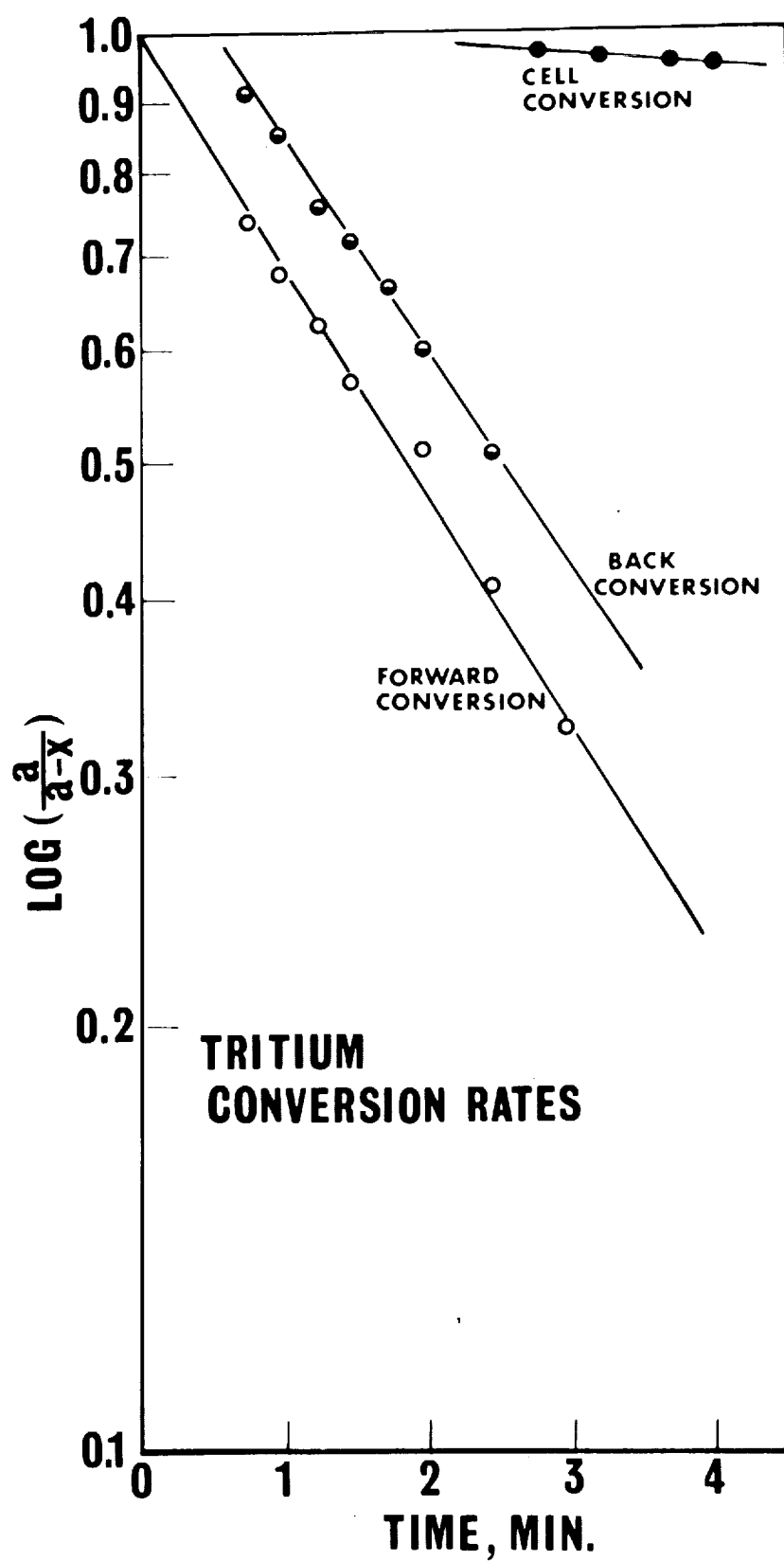


Figure 2

Table I

Equilibrium Ortho-Paratritium Concentrations

T, °K	% Ortho	% Para
0	0.0	100.0
5	0.0	100.0
10	2.8	97.2
15	16.4	83.6
20	33.8	66.2
25	47.4	52.6
30	56.7	43.3
40	66.8	33.2
50	71.3	28.7
75	74.5	25.5
100	74.9	25.1

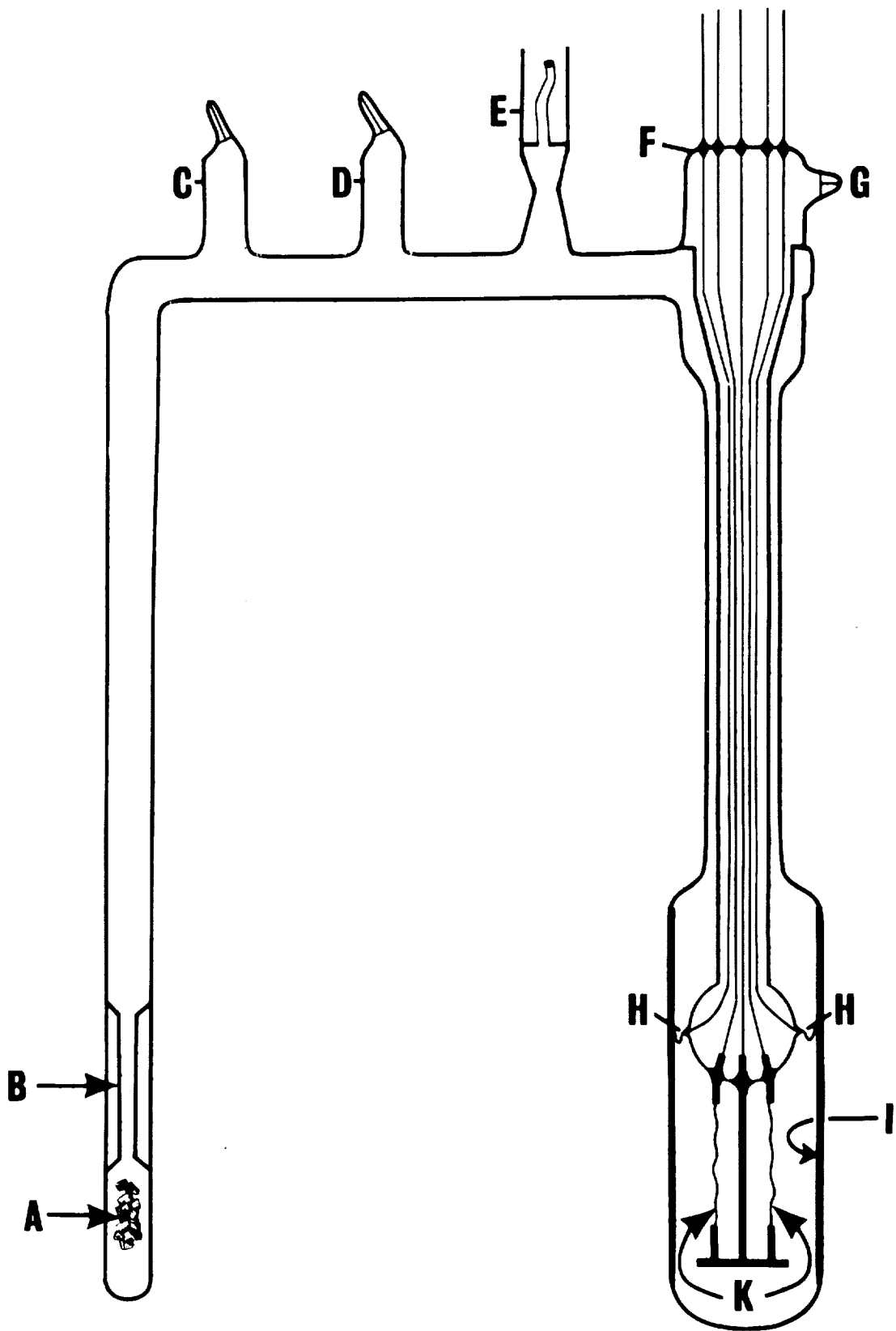


Figure 3

The heat conductivity cell shown in Figure (1) was later modified, replacing the 22 gauge tungsten with 38 gauge copper wires and two micron Wollaston wire as mentioned above for the study of ion removal in an electric field. The new arrangement was identical to that in Figure (1) except that the heat conductivity cell was an exact duplicate of that in Figure (3) without the two additional electrodes (platinum strips) for maintaining an electric field.

Results and Discussion

Conversion on Coconut Charcoal

In Figure 2 the kinetic data for the forward and back conversions on coconut charcoal are shown; the half lifetime for the forward process at 27.16°K being 0.92 minutes and for the reverse at 77.4°K, 1.0 minutes. The forward process was measured by adsorbing the tritium gas at the temperature of liquid nitrogen, where it becomes equilibrated to its normal ratio of 3:1. In transferring from liquid nitrogen to liquid neon, the neon temperature was reached in a few seconds. At the end of the predetermined time of the conversion the bulb was heated with hot water, the tritium gas desorbing in a few seconds. The tritium does not desorb until the temperature is above 77.4°K and therefore there is a back conversion occurring during these few seconds of heating. The degree of back conversion depends on the paratritium concentration, but the fact that the forward conversion data goes through the origin for time, $t = 0$ and follows a straight line on the semi-log plot indicate that these transient times must have been negligible. Considerable scatter was observed for runs where the conversion approached the equilibrium values and this could be explained as back conversion occurring during heating. These points correspond to ordinate

values of 0.1 to 0.01 on Figure 2 and were not included because of the lack of reproducibility.

The adsorption on charcoal at liquid nitrogen temperatures takes about one minute as was readily observed using the heat conductivity cell as a Pirani gauge. From Figure 2, it can be seen that the curve for the back conversion is displaced from the origin by about one minute. By changing the experimental procedure this time could be minimized, but such changes would involve other more serious problems.

When the apparatus was designed provision was made to include a catalyst of gadolinium chloride coated charcoal which was an order of magnitude faster due to its high paramagnetic susceptibility than the normal charcoal in the event that the tritium converted very slowly. The conversion rate on normal charcoal, however, was faster than anticipated and convenient for experimentation. It was found that the gadolinium coated charcoal catalyst was too effective, because even during the fast heating for desorption it was so rapidly re-equilibrated that practically normal tritium desorbed.

From the experimental results of L.Farkas and H.Sachsse⁽¹⁰⁾

(10) L. Farkas and H. Sachsse Sitzber. Preuss. Akad. Wiss. 268 (1933); Z. f. physikal. Chemie, B, 23, 1, 19 (1933).

the surface paramagnetism of diamagnetic charcoal was clearly established as the reason for the fast conversion. To achieve this catalysis the

hydrogen molecules had to diffuse freely even at low temperatures (20.4°K) on the inhomogeneous charcoal surface in order to interact with the paramagnetic centers of the charcoal.

The conversion of ortho-parahydrogen produced by oxygen gas which is paramagnetic has, according to E. Wigner⁽¹¹⁾ the ortho-para

(11) E. P. Wigner, Z. f. physikal. Chemie, B, 19, 203 (1932).

transition probability given by:

$$W_{01} = \frac{8\mu_i^2\mu_j^2 I\pi^2}{h^2 r_s^6 kT} \quad (1)$$

where μ_i and μ_j are the magnetic moments of the interacting species (oxygen and hydrogen); I , the moment of inertia of the converting species; h , Planck's constant; k , Boltzmann's constant; r_s , the collision distance between the i th and j th particles; and T , the absolute temperature. A similar relation can be assumed as a first approximation for the heterogeneous conversion. The rate of conversion is proportional to the product of the transition probability and in the $J \rightarrow J + 1$ transitions a factor considering the endothermicity. (For details see A. Farkas, reference⁽¹²⁾ . The total temperature effect

(12) A. Farkas, "Orthohydrogen, Parahydrogen and Heavy Hydrogen", Cambridge Univ. Press, London 1935.

adsorbed hydrogen is at present not well known. It appears, however, from Figure (2) that the conversion rate for tritium is temperature independent to a first approximation.

Since the ratio I_{H_2}/I_{T_2} is one-third and the ratio of the magnetic moments of tritium and hydrogen is 1.07 (2.79, H_2 ; 2.98, T_2)⁽¹³⁾

(13) H. L. Anderson and A. Novick, Phys. Rev. 71, 372 (1947); F. Bloch, A.C. Graves, M. Packard and R.W. Spence, *ibid.*, 71, 373, 551 (1947); E. B. Nelson and J.E. Nafe, *ibid.*, 75, 1194 (1949).

the ratio of rates of conversion for tritium should be 3.43 times faster in the gas phase compared with normal hydrogen according to equation (1), if converted with a paramagnetic gas such as O_2 or NO . The heterogeneous conversion of tritium on the same coconut charcoal under the same experimental conditions had a half lifetime of one minute which was 27 times faster than the conversion of normal hydrogen or eight times faster than expected if equation (1) for the gas phase were applicable. Three possible reasons for this fast conversion rate are immediately apparent:

(a) The term r_s^6 could be smaller for tritium than for hydrogen because the tritium has a zero point energy which is $(1/3)^{1/2}$ smaller than that of hydrogen. But it seems unlikely that the distance r_s for tritium would be smaller by $(1/8)^{1/6}$ (or a factor 0.7) than the distance r_s for hydrogen. The factor 8 can not be explained by this effect, but it could contribute to a minor extent.

(b) An increase of the rate of conversion by ion interaction or by ion exchange mechanism initiated by the radioactivity of tritium has to be considered. Since carbon is a semi-conductor, any highly efficient chain mechanism is not likely. The deuterium conversion on charcoal where ions cannot be present also was relatively faster than expected as will be shown below.

(c) The explanation for the relatively fast conversion of deuterium and tritium may be due to the fact that a more favorable energy

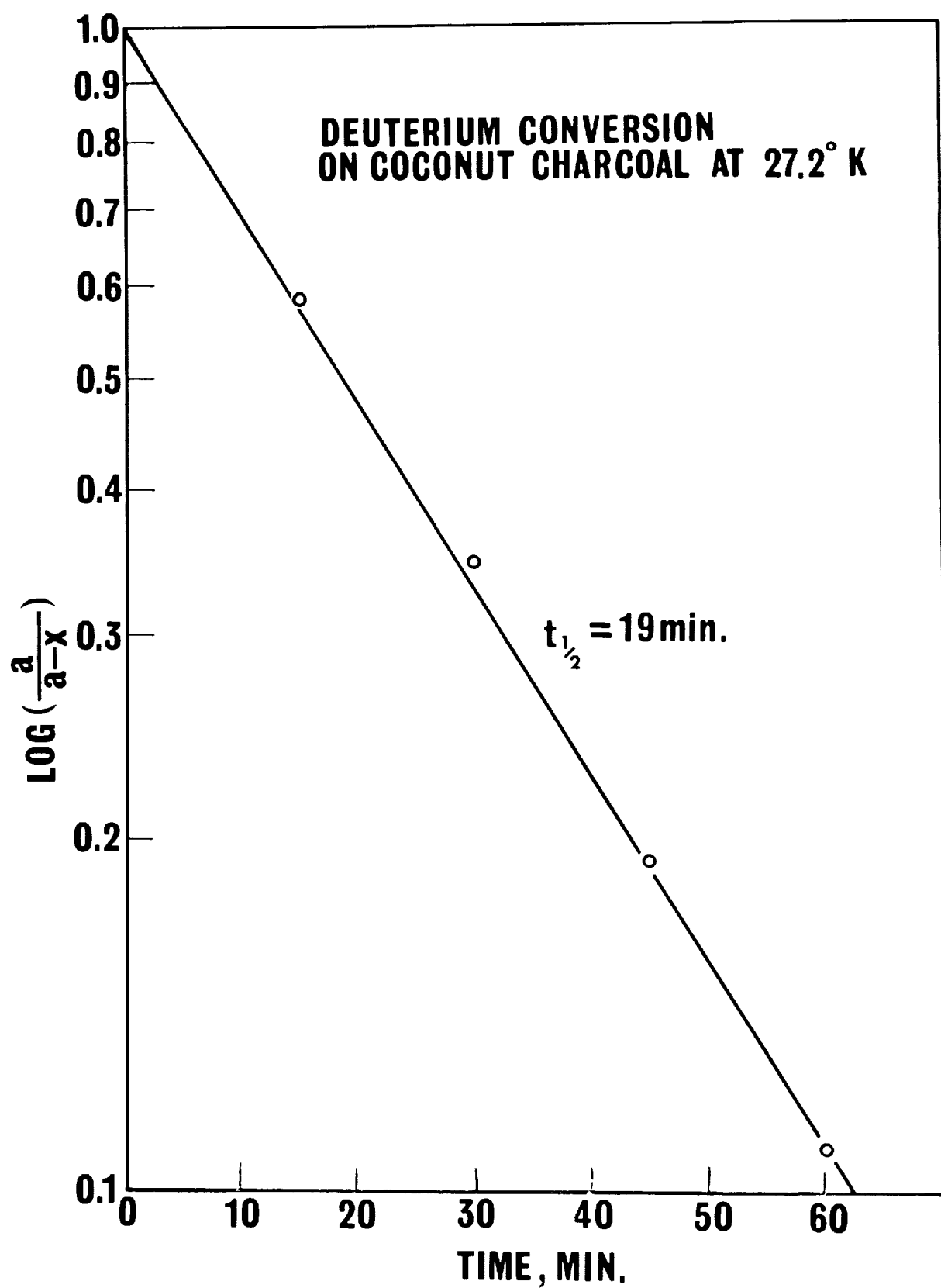


Figure 4

transfer may occur for the tritium. Additional information was obtained by studying the conversion rate of deuterium on the same charcoal under identical conditions. In Figure (4) the kinetic data for the conversion of deuterium are reported; the graph represents the fractional decrease in paradeuterium normalized between room temperature and 27.2°K as a function of time. The measurement of the slope yields a half lifetime of 19 minutes. If one considers the half lifetime for hydrogen, deuterium, and tritium with due allowance being made for difference in the nuclear magnetic moment an interesting relationship becomes apparent. In Table II it may be seen that deuterium and tritium convert four and eight times faster respectively compared to hydrogen under identical conditions. The marked departure of deuterium and tritium may very well be due to a more favorable energy transfer. For the heterogeneous phase here, as well as for the solid phase conversion of tritium reported in the next section, a one phonon emission process seems more likely. Moreover, since the rate for deuterium conversion on charcoal was also faster than anticipated and in this case obviously no ions are present, the effect of ions in the case of tritium conversion on the charcoal should be at the most only minor.

Conversion in Solid Phase

For normal hydrogen it was shown by Bonhoeffer and Harteck⁽⁸⁾ that the ortho-para transformation does not become effective due to a solidification or melting process. Furthermore, Bonhoeffer and Harteck showed that in the liquid phase the change of parahydrogen concentration was about 1%/hr. These studies on the liquid and solid phases clearly established the existence of freely rotating molecules. Subsequently, exact measurements for the transformation in the solid

Table II
Conversion of Hydrogen, Deuterium and
Tritium on Coconut Charcoal

	Observed half lifetime min.	$K_{\text{obs}}, \text{min}^{-1}$	$\frac{(\mu^2 M)_H^*}{(\mu^2 M)_{\text{D or T}}}$	$k_{\text{calc}}, \text{min}^{-1}$	$k_{\text{obs}}/k_{\text{cal}}$
H ₂	27	0.026	1.00	(0.026)	1
D ₂	19	0.036	0.199	0.0051	3.9**
T ₂	1.0	0.69	3.42	0.088	8

*Using Wigner's expression (equation 1) it may be seen that the calculate rate constants for deuterium and tritium relative to hydrogen are proportional to $\frac{1}{(\mu^2 M)_{\text{D or T}}}$ which is the reciprocal of the

product of the square of the nuclear magnetic moment and the mass deuterium or tritium.

**The factor $(3/4)^2$ must be included to account for the unequal nuclear spins of hydrogen and deuterium⁽¹⁴⁾ (H₂ and T₂, $S = 1/2$, D₂, $S = 1$)

(14) F. Kalckar and E. Teller, Proc. Roy. Soc., A150, 520 (1935)

phase were made by Cremer and Polanyi⁽¹⁵⁾. Recently, Motizuki and

(15) D. Cremer and M. Polanyi, Z. f. physikal Chemie, B, 21, 459 (1933).

Nagamiya⁽¹⁶⁾ have treated the conversion in the solid theoretically.

(16) K. Motizuki and T. Nagamiya, J. Phys. Soc. Japan, 11, 93 (1956); *ibid.*, 11, 654 (1956); *ibid.*, 12, 163 (1957).

They find nearly exact agreement between their calculated half lifetimes and the half lifetime of sixty-hours measured by Cremer and Polanyi; this value is 210 times slower compared to the half lifetime value of seventeen minutes for the solid phase conversion of pure tritium reported in Figure (5). According to equation (1) the rate of conversion varies directly with mass of the converting species; therefore the tritium would be expected to be only a factor three faster, rather than the 210 times faster observed. The somewhat unexpected behavior of tritium may however be explained either by a more favorable energy transfer or an ion mechanism. In Table III the Debye characteristic temperature for each isotope and the corresponding rotational temperatures are given. Examination of these data seem to indicate that for hydrogen the minimal energy transfer process must involve the emission of two phonons whereas for tritium a one phonon emission process seems likely. Deuterium, however, may have either one phonon or two phonon process.

Conversion at Neon Temperature in the Gas Phase

A slow conversion of normal tritium to the equilibrium concentration at liquid neon temperature could be observed as shown in

Table III

Energy Transfer Parameters

	Debye Temperature, θ_D^*	Rotational Temperature θ_R^{**} ($J = 0 \rightarrow J = 1$)
Hydrogen	91	172
Deuterium	89	86
Tritium	(72-87)***	57

$$^*\theta_D = \frac{h\nu}{k}$$

$$^{**}\theta_R = \frac{\sigma h^2}{8\pi^2 I k} ; \sigma \text{ denotes the symmetry number; } h, I, \text{ and } k \text{ are Planck's constant, the moment of inertia and Boltzmann's constant respectively.}$$

***The Debye characteristic temperature for hydrogen and deuterium has been measured directly(17,(18)); to our knowledge the Debye characteristic temperature for tritium has not been measured. Since hydrogen and deuterium behave anomalously it is difficult to extrapolate the value for tritium and therefore we give large limits of error.

(17) F. Simon, K. Mendelssohn and M. Ruhemann, *Naturwiss.* 18, 34 (1930).

(18) K. Clusius and E. Bartholome, *Naturwiss.* 22, 526 (1934).

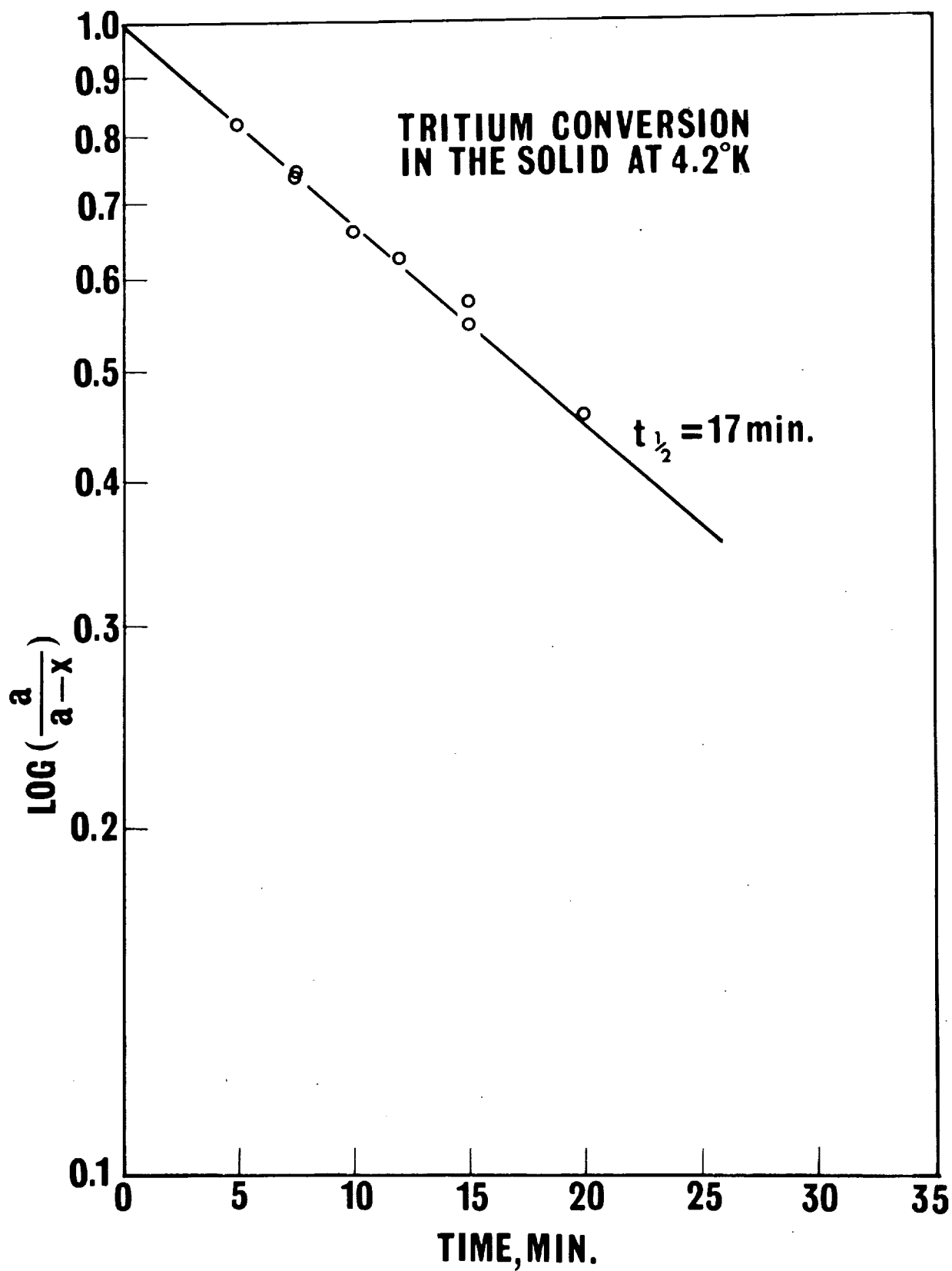


Figure 5

Figure (1). This conversion must have occurred in the neon cooled thermal conductivity cell in the gas phase because under the experimental conditions used, any conversion due to van der Waals adsorption or due to the glass walls should be negligible. Oxygen frozen on the walls is known to cause ortho-para conversion in hydrogen. (For details see A. Farkas, reference (12)). Therefore a platinum wire was heated to 1000°K which would convert even traces of oxygen to T_2O while in liquid N_2 . Subsequent recooling the cell in liquid neon, however, still resulted in exactly the same rate of conversion indicating the conversion was not due to oxygen. Since the liquid neon will freeze all impurities except the hydrogen isotopes and inert helium, the system will be extremely clean and ions produced by the radioactive tritium may have a relatively long chain length causing conversion and only terminated by ion-electron recombination on the wall or in the gas phase.

Tritium atoms resulting from ion-electron recombination cannot cause further conversion over $T + T_2(\text{ortho}) \rightarrow T_2(\text{para}) + T$, analogous to hydrogen, since the heat of activation of $H + H_2(\text{para}) \rightarrow H_2(\text{ortho}) + H$ is found to be 7 kcal⁽¹⁹⁾. This relatively low heat of activation for

(19) A. Farkas, Z. f. Elektrochemie, 36, 782 (1930); Z. f. physikal Chemie, B, 10, 419 (1930); K. Geib and P. Harteck, ibid., Bodensteinband, 849 (1931).

the exchange reaction is due to the zero point energy of the hydrogen molecule and the tunneling effect for this exchange reaction as theoretical analysis has shown. But since the zero point energy of tritium is 2.56 kcal less than in the hydrogen molecule (See Table VI) and the tunneling effect in the case of tritium exchange reactions is almost

negligible, and therefore the apparent heat of activation will exceed the value of 7 kcal; but even 7 kcal would suppress any reaction at 27.2°K even an activation energy of 7 kcal would suppress any reaction.

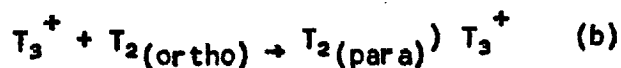
In the course of our experimentation a series of experimental arrangements filled with tritium were used with somewhat different heat conductivity cell designs. Each cell had characteristic rates for conversion which could be reproduced; the rate of conversion approximated first order. Since conversion by atom reactions and paramagnetic conversion by oxygen has to be disregarded, ion reactions were considered to explain this conversion.

The primarily formed T_2^+ ion may react with T_2 :



which is analogous to the hydrogen ion reaction expected with hydrogen⁽¹⁹⁾.

The T_3^+ ion can then bring about conversion via:

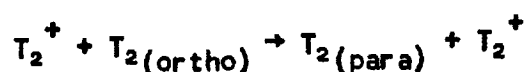


which may occur with a long chain length before destruction of the T_2^+ ion.

The conversion is at equilibrium at the neon temperature of the cell, which was confirmed by observing the conversion of pure para-tritium, and normal tritium; both converting to the one to one equilibrium mixture at neon temperature. Since the equilibrium is attained at 27.2°K, there can be no heat of activation associated with reactions occurring.

If reactions (a) or (b) should have a heat of activation of only one kilocalorie, which would not be observed at room temperature under the condition here of 27.2°K, the reaction could not occur before ion-electron recombination. It should be noted that if a heat of activa-

tion of about 1 kcal. or more should exist for reaction (a) then the T_2^+ could not react with T_2 and might be the chain carrier via



The ion effect will dominate in the cell cooled with liquid neon since the particle density of tritium is, at 27.2°K, ten times that at room temperature. Not only is 70 to 90% of T_2 in the cell, but ions producing conversion will be in much higher concentration at the low temperature because of the ten times greater concentration of tritium. The ion production will increase proportional to the density of the number of particles of radioactive tritium which disintegrate, and proportional to the cross-section or particle density of tritium in this pressure range. Further the recombination of the ions will also be less at neon temperature because diffusion to the wall where recombination occurs is decreased by the higher particle density and the low temperature. The recombination in the gas phase is minor because of the relatively rapid diffusion to the wall not only of the positive ions but especially of the electrons before they are thermalized. An electric field was applied across the cell using internal platinum electrodes. The current measured indicated about 10% of the beta energy released in the gas phase. The chain length then is in the order of 10^5 .

Changes in the characteristics of the wall could be expected to be more or less effective in destroying the ions. It was found that faster conversion occurred in a system mainly of glass, while one with platinum electrodes (to measure the effect of electric field) was considerable slower. See Table IV. The glass walls of the cell could repel or reflect a fraction of the ions on collision where the metal

Table IV

Observed Half Lifetimes
For the Different
Heat Conductivity Cells

Cell Description	Observed Half Lifetime min.
Minimum Metal Surface	15
Tungsten leads Extending throughout cell envelope (Figure 1 first cell used)	60
Platinum electrodes without Voltage applied (Figure 3)	27
Platinum electrodes with Voltage applied (Figure 3)	33

surfaces would recombine the ions with a higher recombination efficiency. It would be possible by these techniques to obtain an insight into the recombination characteristics of ions for different surfaces at these low temperature. Research on these lines are in progress. Thompson and Schaeffer⁽²⁰⁾ have proposed an ion chain mechanism for hydrogen and

(20) S. O. Thompson and O. A. Schaeffer, J. Am. Chem. Soc., 80, 553 (1958); Radiation Research, 10, 671 (1959).

deuterium exchange when subjected to alpha radiation, where the gases were very clean. Long chains could be obtained since charge transfer reactions with an impurity with a lower ionization potential was avoided, which obviously terminated the chain. Under the conditions used in the present work, the liquid neon quantitatively froze out all interfering gas impurities. Therefore, charge transfer reactions with an impurity with a lower ionization potential is also avoided.*

In the ion chain mechanism of Thompson and Schaeffer for the exchange between hydrogen and deuterium certain steps of the chain must have a heat of activation because the different species have different amounts of zero point energy; these reactions could not be expected to occur at 27.2°K. In our case, however, there is the distinct possibility to observe a reaction chain, where each link of the chain is operative without any heat of activation and the length of the chain is then determined by the rate of consumption of the ions which may be due to recombination in the gas phase or on the walls.

*More exact measurements of the ion production under various experimental conditions are in procedure.

In a mixture of hydrogen and tritium the slow gas phase conversion could not be observed for the tritium and it was postulated that a chain termination step might occur. The reaction, $H_2^+ + T_2 \rightarrow H_2 + T_2^+$ would be endothermic to the extent of 1.24 kcal considering the differences in zero point energy; hence, at 27.2°K reaction would not occur. Table V shows similar reactions and their corresponding heats of reaction calculated according to the zero point energies listed in Table VI. All of these reactions are endothermic and will not occur before ion recombination at 27.2°K under our conditions.

The triatomic ions H_3^+ , H_2T^+ , HT_2^+ and T_3^+ may also interact with H_2 , HT and T_2 . The zero point energies of these ions are not known, but the differences should be analogous to those indicated for the diatomic ions. It means they may have relatively lower vibrational frequencies per degree of freedom than the uncharged diatomic species; also, the sum of the zero point energies will decrease with the tritium content of these species. All reactions involving a triatomic ion and uncharged diatomic molecules will tend therefore to go in the direction where the triatomic ions contain preferably hydrogen, and in the diatomic molecules preferably tritium. Consequently, ortho-paratritium conversion over long chains will not occur. Since the ions resulting from these reactions would not be tritium ions, but mixed ions or hydrogen ions, neither the hydrogen - tritium exchange nor the ortho-paratritium conversion could occur.

Gas Phase Conversion in the Presence of a Paramagnetic Gas

According to the formula of Wigner a paramagnetic gas can cause conversion of parahydrogen to orthohydrogen. The relative magnetic moments of hydrogen and deuterium were determined in this manner

Table V
Hydrogen, Deuterium and
Tritium Ion Reactions

$H_2^+ + T_2 \rightarrow H_2 + T_2^+$	$\Delta E_0^0 = +1.21 \text{ kcal}$
$H_2^+ + T_2 \rightarrow HT + HT^+$	$\Delta E_0^0 = +0.28$
$H_2^+ + HT \rightarrow H_2 + HT^+$	$\Delta E_0^0 = +0.51$
$HT^+ + T_2 \rightarrow HT + T_2^+$	$\Delta E_0^0 = +0.70$
$H_2^+ + D_2 \rightarrow H_2 + D_2^+$	$\Delta E_0^0 = +0.84$
$H_2^+ + D_2 \rightarrow HD + HD^+$	$\Delta E_0^0 = +0.53$
$H_2^+ + HD \rightarrow H_2 + HD^+$	$\Delta E_0^0 = +0.38$
$HD^+ + D_2 \rightarrow HD + D_2^+$	$\Delta E_0^0 = +0.45$

Table VI

Zero Point Energies*, kcal

H ₂	6.20
HD	5.38
HT	5.09
D ₂	4.41
DT	4.01
T ₂	3.62
H ₂ ⁺	3.24
HD ⁺	2.80
HT ⁺	2.64
D ₂	2.29
DT ⁺	2.09
T ₂ ⁺	1.87

*These values were calculated from the spectral data reported by Herzberg⁽²¹⁾.

(21) G. Herzberg "Molecular Spectra and Molecular Structure", Vol. I, D. Van Nostrand Company, Inc., New York 1950.

by using oxygen as a paramagnetic gas⁽¹⁰⁾ and observing the rates of conversion of ortho-para systems. Similarly we have observed the same type of relative conversion rates for hydrogen and tritium using nitric oxide in this case as the paramagnetic gas. Oxygen would combine with the radioactive tritium in a relatively short time.

Nitric oxide was used for ortho-para conversion of hydrogen⁽¹⁰⁾. Of the lowest states of NO the $^2\Pi_{3/2}$ is 345 calories above the $^2\Pi_{1/2}$ ground state. The upper state is paramagnetic whereas the lower state is not. Therefore, at room temperature a high percentage of the NO is paramagnetic while at liquid neon temperatures it is not only frozen out, but over 99% of the NO will be in the lower diamagnetic state.

The observed half lifetime of 17 minutes for a partial pressure of 100 mm of NO was within 10% in agreement with the prediction of Wigner's formula, equation (1); thus, this result adds support to the validity of this equation for gas phase conversion, where the r_s is assumed unchanged.

Conclusions

In the proceeding paper⁽⁷⁾ we have shown that it is possible to convert normal tritium to paratritium on charcoal in the temperature region of liquid neon and liquid helium. Hydrogen and tritium have the spin 1/2 and follow therefore the same statistics. In addition they have almost the same nuclear magnetic moment. It is therefore of major interest to compare the kinetic data of the ortho-para conversion of these two hydrogen species. From the results obtained, we have been able to show that

(1) On a coconut charcoal under the same conditions the ortho-para transformation of tritium was 27 times faster than that of normal hydrogen.

(2) Concerning the transformation rate in the solid phase the ortho-paratritium transformation has a half lifetime of 17 minutes which is 210 times faster as compared with the rate of transformation of normal hydrogen.

(3) Concerning the occurrence of transformation reactions by ions the following conclusions could be made:

(a) During the transformation experiments in the gas phase the heat conductivity cell remained always cooled with liquid neon; therefore the tritium gas was extremely pure. It seems that under these conditions ion exchange reactions occur with practically zero heat of activation and with large collision cross-sections.

(b) Metal surfaces enhanced the ion recombination process, thereby decreasing the rate of conversion;

(c) The application of an electric field in a limited part of the cooled experimental arrangement takes out the ions and therefore decreases the rate of conversion;

(d) In the adsorbed phase on charcoal (which is a semiconductor) ions do not seem to play a role in the catalysis;

(e) In the solid phase we would not like to commit ourselves at the present time as to whether ions play a role for the conversion or not.